Detection of defect-induced magnetism in low-dimensional ZnO structures by Magnetophotocurrent

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The detection of defect-induced magnetic order in single low-dimensional oxide structures is in general difficult because of the relatively small yield of magnetically ordered regions. In this work we have studied the effect of an external magnetic field on the transient photocurrent measured after light irradiation on different ZnO samples at room temperature. We found that a magnetic field produces a change in the relaxation rate of the transient photocurrent only in magnetically ordered ZnO samples. This rate can decrease or increase with field depending whether the magnetic order region is in the bulk or only at the surface of the ZnO sample. The phenomenon reported here is of importance for the development of magneto-optical low-dimensional oxides devices and provide a new guideline for the detection of magnetic order in low-dimensional magnetic semiconductors.

The detection of low levels of magnetic moment is of importance for the study of new materials and new phenomena in solid state magnetism. New technologies such as the simultaneous use of a superconducting quantum interferometer device (SQUID) and the Moke effect, are being developed to detect low levels of magnetic signals[1]. This development is of particular interest for the study of materials that show magnetic order at surprisingly high temperatures due to a relatively high concentration of defects, like vacancies[2]. Defect-induced magnetism (DIM) in semiconducting materials, especially oxides, is of interest also because of the expected advantages one has combining optical and semiconducting properties for spintronics applications. However, at present there are several difficulties, partially in the reproducibility of the DIM due to the unknown systematic preparation of the necessary defects density, and also because of the low levels of magnetic signal due to the small amount of magnetically ordered regions in a sample.[3,4]

It has recently been shown that the photocurrent is sensitive to the minority carriers at the interphase between two semiconductors and it can be changed by an external magnetic field, opening new possibilities to design new devices based on photocurrent processes and interphases properties[5]. On the other hand, it has been observed that the photocurrent can be affected by relatively low applied fields of the order of 0.5 T or less, in diluted magnetic semiconductors at room temperature thanks to the exchange interaction[6]. However, little attention has been drawn to persistent photocurrent phenomena and their sensitivity to the variation of the oxygen absorption after photoexcitation[7,8]. Such photocurrent phenomena are of interest to study the effect of external magnetic fields on photo-transport mechanisms at the surface and/or in bulk of defect-induced magnetic oxides.

There is consent nowadays that the photocurrent in ZnO is mainly a surface effect[9]. The model generally used to understand photocurrent effects is based on the desorption and absorption of oxygen at the ZnO surface. Oxygen from the environment are chemisorbed at the surface and are negatively charged by capturing a free carrier, producing at the same time a depletion zone or surface band bending[10]. During UV-illumination electron-holes are created. The electrons are promoted to the conduction band and the holes from valence band and/or intraband donor defects such as oxygen vacancies (V_O) and O interstitials (O_i)[10], can migrate to the surface to discharge the oxygen at the surface. This produces its photodesorption and decreases the band bending, allowing the free carrier to diffuse in both directions, i.e. from bulk to surface and vice versa. After turning off the light excitons are recombined and the oxygen chemisorbed at the surface captures a free carrier, reducing the free carrier density and reestablish finally the initial dark state.

The oxygen reabsorption at the surface provides the main contribution that affects the transient photocurrent. It depends on the environmental oxygen concentration and inversely on the rate of recombination of electrons at traps centres[11]. In this work we studied in detail the effect of a magnetic field on the transient photocurrent produced after turning off the light. The presented results indicate that the influence of an external magnetic field on the transient photocurrent is observed only in samples with defect-induced magnetic order. The effects are detectable thanks to the sensitivity of the phototransport processes. They help to detect the existence of magnetic order at high temperatures in low-dimensional ZnO structures, as single nano/microwires or microstructured thin films, which would remain undetectable by standard techniques.

I. METHOD

For the photocurrent measurements we used four different ZnO samples. Three samples were 300 nm thin films grown on 6 × 6 mm^2 *a*-plane Al_2O_3 substrates by Pulsed Lased Deposition (PLD). Two different films were grown, one in oxygen atmosphere (ZO) and another in nitrogen (ZN) enviroment with partial pressures of 1.73×10^{-2} mbar from a base vacuum of 10^{-7} mbar[12]. The ZO film was treated afterwards with hydrogen plasma (ZOH) ($\approx 10^{18}$ H^+/cm^2 at an energy of 300 eV at room temperature)[13]. All samples were patterned to a size of $\sim 10 \times 5$ μm^2 by e-beam lithography and wet-etching techniques[14].

The fourth sample was a single ZnO microwire with a diameter of 10 μm and 200 μm length. The wire was doped with Li (5%) and treated with hydrogen plasma (ZLH) in a similar way. Previous studies revealed that the room temperature hydrogen-plasma treatment in Li-doped ZnO samples (Li-concentration $\geq$ 3%) produces Zn-vacancies (V_{Zn}) in 10 nm depth from the wire surface. The used procedure produces a V_{Zn} concentration similar to the Li one and magnetic order can be observed at room temperature, as revealed by XMCD and SQUID techniques[15].

The magneto-photocurrent measurements were performed in a home made close-cycle cryostat with the possibility to apply a magnetic field of 0.4 T. The field was always applied parallel to the input current direction, also parallel to the main film area or the main axis of the microwire. During the measurements the samples were kept always at $5x10^{-3}$ mbar to ensure a constant oxygen partial pressure at 305 K. To prove the importance of the oxygen partial pressure in the persistent photocurrent relaxation, we performed similar experiments after purging the chamber with He to reduce the partial pressure of oxygen. The reduction of the oxygen partial pressure in the chamber increased the photocurrent relaxation time by several hours, in agreement with previous reports[16]. It points out the importance of the oxygen absorption for the persistent photocurrent process. The light irradiation was done using a Xenon lamp coupled to a monochromator from which we selected a wavelength of $\lambda = 370$ nm for all experiments.

II. RESULTS

The methodology used to obtain the change of the transient photocurrent on time and under a magnetic field consists of measuring consecutively several light-on/off cycles of the photocurrent. In such an experiment the samples are illuminated until the photocurrent increases to a previously selected value i_{ON} different from saturation. After reaching it, the light is turned off and the transient photocurrent decreases. When it reaches a previously selected value i_{OFF}, see Fig. 1, the light is turned on till the photocurrent reaches i_{ON}. The time Δt

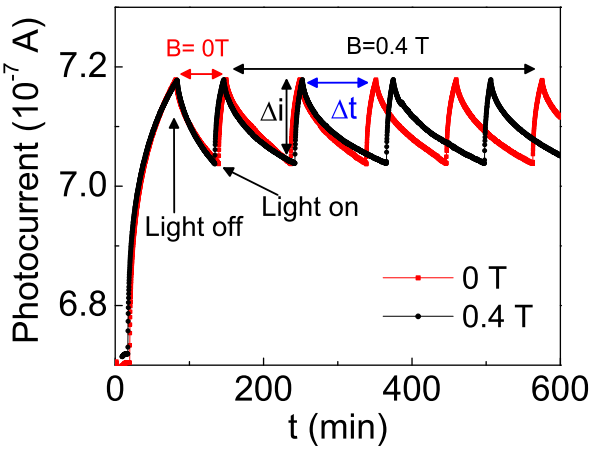

FIG. 1. Experimental method to measure the effect of an external magnetic field on the transient photocurrent. The two curves represent the cycles measured at $B = 0$ T and $B = 0.4$ T of ZN thin film

for every transient photocurrent cycle was measured for a previously fixed $\Delta i = i_{ON} - i_{OFF}$. The same procedure is repeated several times to obtain the time dependence of the transient photocurrent rate (TPR) defined as $\frac{\Delta i}{\Delta t}(t)$. The first cycle performed in every measurement is done at zero magnetic field (B) to ensure an equal starting state for every measurement of the same sample. Note that the selected Δi depends on the sample because the photocurrent varies for every sample.

To check the equipment performance and the reproducibility of previously published variation of the TPR with magnetic field[7], we have measured the ZN film, which shows magnetic order at room temperature due to the existence of V_{Zn} produced during preparation (see inset in Fig. 2(a))[12]. The cycles measured for the ZN sample at zero and 0.4 T field are shown in Fig. 1. For both fields we observe that there is an increase of Δt after every cycle. This is due to an increase of the number of traps(holes) created during photoexcitation[17]. Since not all the holes are recombined during the light is off an additional number of photo-generated holes are produced every cycle. The larger the number of holes the larger the exciton recombination rate, which implies that the number of carriers moving from bulk to surface, necessary to initiate the oxygen reabsorption and reestablish the initial dark conditions, reduces. Thus, the TPR decreases with time, see Fig. 2(a).

When an external magnetic field is applied, we observe qualitatively a similar variation for the TPR to the one observed at zero field, see Fig. 2(a), however, the variation of Δt is larger. It means there is an increase of the transient photocurrent time due to the effect of the external magnetic field, which should be related to a reduction of the oxygen absorption rate in comparison to the zero field state. The observed behavior is in good

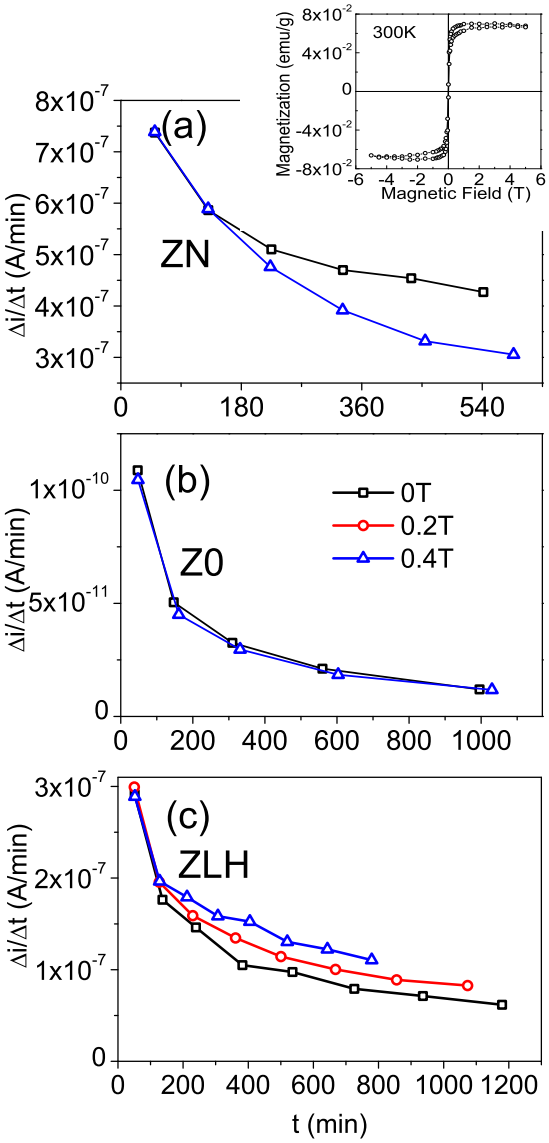

FIG. 2. Variation of the transient photocurrent rate at different applied magnetic fields, as a function of the total time for the thin film samples (a)ZN and (b) ZO and the single microwire (c) ZLH. All measurements were done at a fixed temperature of 305 K. The inset in (a) shows the field loop of the magnetization measured for the ZN film at 300 K.

agreement with that reported previously[7].

After observing the magnetic field effect on the TPR of a magnetic sample, a ZO thin film was measured, which does not show any sign of magnetic order at room temperature. The TPR(t) results shown in Fig. 2(b) indicates that there is no dependence with the external magnetic field.

To gain a deeper insight into the field dependence of the TPR we compare the obtained results with those from a sample that shows magnetic order only within a surface shell, instead of a bulk magnetic sample such as in

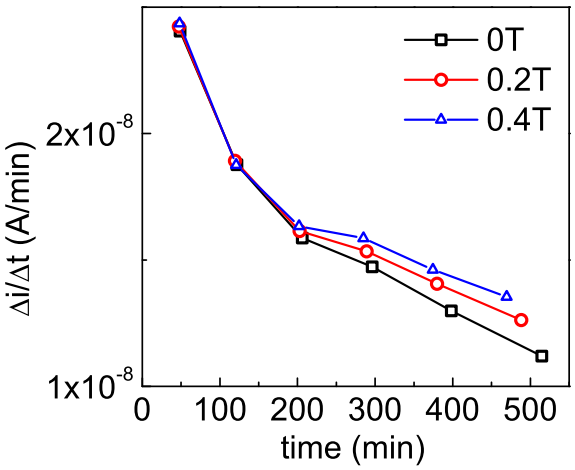

FIG. 3. Time dependence of the transient photocurrent rate for ZOH film, at different applied magnetic fields at 305 K.

ZN. The implantation of H^+ in the ZLH sample produces a significant amount of defects within a 10 nm surface region[13,15]. Different experimental methods including XMCD as well as numerical calculations indicate that the produced concentration of $V_{\rm Zn}$ ($\sim 5\%$) near the Li ions is the reason for the magnetic order at room temperature[15]. The results for ZLH are shown in Fig. 2(c). In contrast to ZN, the TPR increases with magnetic field.

Because the results indicate that the TPR can depend on the applied magnetic field only for magnetically ordered samples, we implanted 10^{18} H^+/cm^2 in the non-magnetic ZO thin film shown in Fig. 2(b), labeled now ZOH. Such implantation of H^+ can produce a near surface magnetic layer within $\simeq 10$ nm, similarly to the one observed in ZnO single crystals[13]. The results of the TPR for this sample are shown in Fig. 3. The observed variation with field is similar to the one observed for the ZLH microwire suggesting that its origin should be related to the formation of a magnetically surface shell. It is worth to note that the amount of magnetically ordered mass in this sample is too small to be measurable with a commercial SQUID, i.e. its ferromagnetic moment at saturation is smaller than 2×10^{-7} emu. Nevertheless, the photocurrent is influenced by the thin magnetic layer emphasizing the sensitivity of this property to magnetic order produced by defects in this case.

To understand qualitatively the observed phenomenon we take into account the role of the induced magnetic order in the bulk and at the near surface region. In both cases we have the Zeeman splitting produced by the finite magnetic field, as consequence of the spin-orbit $(L-S)$ coupling with the magnetic defects, $V_{\rm Zn}$, which is large for wide band gap magnetic semiconductors[18]. Due to optical selection rules, which accompany the Zeeman splitting and where the spin orientation of the magnetic defects plays a role[19], the trapping probability of conduction electrons by the defects increases with field.

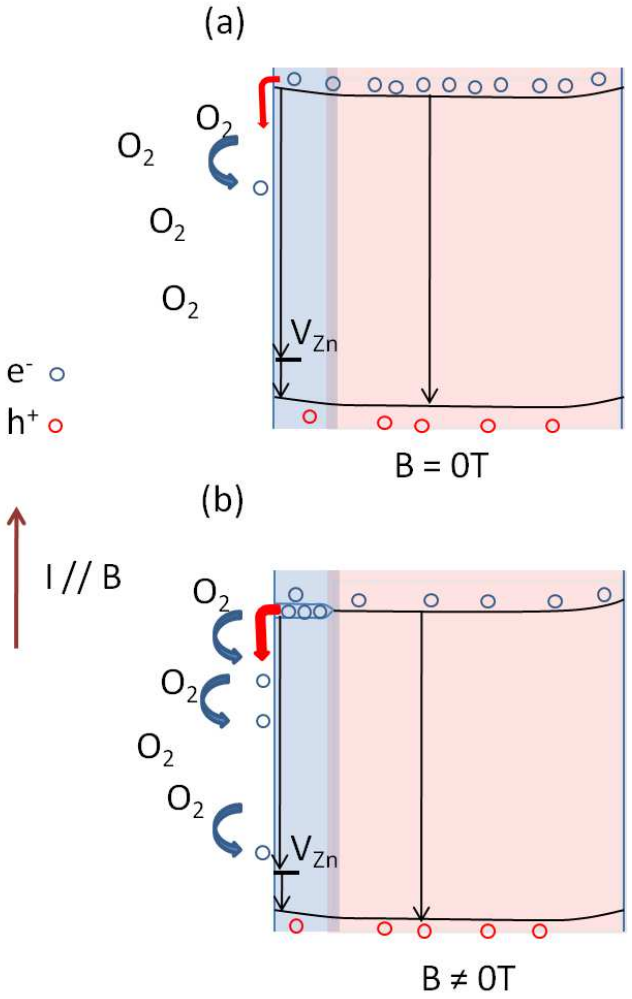

FIG. 4. Sketch of the magnetically ordered near surface region of a low-energy H^+ implanted ZnO sample, at $B = 0$ T (a) and at B≠0 T (b). The magnetic field is applied parallel to the input current I. The blue surface region of thickness $\sim$ 10 nm, denotes the defect-induced magnetically order region and the pink part is the non-magnetic bulk region. Under a magnetic field the magnetic region shows a band splitting due to the Zeeman effect, changing the probability of carrier accumulation at the surface and influencing the transient photocurrent rate. The Zeeman splitting is not in scale with the drawn energy gap.

This effect reduces the amount of electrons that can reach the surface and capture oxygen from the environment to reestablished the initial dark conditions. In this case the TPR decreases with applied magnetic field, see Fig. 2(a).

In the second case, observed for samples ZLH and ZOH, we must consider the heterostructure with only the near surface region magnetically ordered, see Fig. 4. When an external magnetic field is applied, similarly to the first case, a Zeeman splitting occurs in the magnetic region. This energy shift leads to a redistribution of carriers with larger probability to be at the deeper potential. In this case and just after removal of the light excitation, a larger accumulation of electrons occurs at the magnetic region due to the carriers coming from the non-magnetic bulk region. Therefore, more electrons reach the surface increasing the probability for oxygen trapping at the surface and as consequence a faster TPR[20] is observed.

The presented results clearly indicate a dependence of the TPR with relatively low magnetic fields at room temperature. This magnetic field dependence is qualitatively different for ZnO samples with magnetic order in the bulk or at the near surface region. The observed change in the TPR is related to the variation of the rate of oxygen absorption to reach the initial dark state. This oxygen absorption rate depends on the number of free electrons reaching the surface, and their amount depends on magnetic field and the magnetically ordered region in the sample. Our results indicate that low fields can be used to tune the transient photocurrent in magnetic samples, which can be useful to detect sensitively room temperature magnetic order in low-dimensional systems, a magnetic order that may remain undetectable using routine techniques such as SQUID.

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